LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Germanium nanocrystals synthesized in high-boiling-point organic solvents.

N. Zaitseva, Z. R. Dai, J. Harper, C. Saw

December 15, 2006

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Germanium nanocrystals synthesized in high-boiling-point organic solvents.

N. Zaitseva, Z.R. Dai, J.Harper, and C. Saw.

Abstract. Ge nanoparticles with sizes from 1 to 15 nm were synthesized by thermal decomposition of germane precursors: trichlorogermane (TCG), tetraethylgermane (TEG) and tetrabutylgermane (TBG). Experiments were performed using organic solvents, trioctylamine, squalene and octacosane with high boiling points, in the temperature range of 380°C to 430°C. It was shown that high-yield elemental Ge can be obtained from TCG decomposition at relatively low temperatures, above 140°C. However, below 380°C, the final product of decomposition consists mainly of amorphous nanoparticles. Homogeneous formation of uniform Ge nanocrystals was obtained at the temperatures above 400°C. The use of organic solvents extended the temperature range of reactions thus enabling experiments to be conducted with additional precursors, TEG and TBG, not used previously in colloidal synthesis because of their high decomposition points. Characterization by transmission electron microscopy showed that, depending on reaction temperature, the final products of these precursors decomposition consists of Ge nanocrystals or nanowires that grow only in one <110> direction.

Introduction.

Intensive studies of quantum confinement effects in semiconductors have stimulated rapid development of synthesis techniques to produce nanoscale materials, among which Si and Ge have specific importance because of their possible integration into Si-based light-emitting devices. Different methods to produce colloidal Ge nanocrystals (NCs)

include metathesis reactions using Zintl salt,[1,2] crystallization in inverse micelles,[3] reduction of CCl_4 with various reduction agents,[4-7] and thermal decomposition of organogermanes.[8-10] Recent development of synthesis techniques goes in the direction of producing NCs in the larger quantities[7,10,11] needed for comprehensive studies of their structural and optical properties. In this respect, the syntheses in temperature-pressure reactors [8-10] operating at elevated temperatures seemed to be the most promising approach to obtain macroscopic amounts of Ge NCs. The possibility of reaching high-temperatures above 400°C needed for decomposition of organosilanes and formation of highly crystalline Ge is an advantage of these methods. At the same time, formation of precursor and solvent decomposition byproducts, which remain inside the closed pressure reactors often produces difficulties in complete separation and purification of final NCs.[10] Identification of new precursors that readily decompose at lower temperatures[11] enables this problem to be overcome, returning Ge NC synthesis to the classical wet-chemistry method[12] well-proven for production of macroscopic amounts of colloidal nanoparticles with controlled size and narrow size distribution. Additional benefits in the synthesis of colloidal nanoparticles can be introduced by the use of more appropriate solvents with higher boiling points. Among the most widely used coordinating solvents, such as TOPO (tri-n-octylphosphine oxide), TOP (tri-n-octylphosphine), and TBP (tri-n-butylphosphine), TOPO has the highest boiling point, 360°C, which limits the use of broader varieties of precursors known to produce elemental Ge upon their decomposition at higher temperatures. Here we report the results of experiments made with alternative solvents, tri-n-octylamine (TOA, $C_{24}H_{51}N$), squalene ($C_{30}H_{62}$), and octacosane ($C_{28}H_{58}$), which have higher boiling points in the range of 380-430°C. The goal of this work was to

2

study conditions of Ge NC formation by decomposition of trichlorogermane (TCG) and more traditional germanoalkyls, tetraethylgermane (TEG) and tetrabutylgermane (TBG), used as initial precursors.

Experimental Section.

<u>Syntheses</u> were conducted in a standard 100-ml, three-neck, heavy-wall Pyrex flask connected to a vacuum/inert gas (Schlenk) line. In a typical experiment, 15 g of TOA (Aldrich, 98%), squalene (Aldrich, 98%), or octacosane (Aldrich, 99%) were introduced into the flask at room temperature and evacuated to a level below 100 mTorr. To remove any traces of water, evacuation continued at 110^oC for 30 min, and then the flask was heated to the experimental temperature of 380-430°C under continuous Ar flow. Precursor mixtures of TCG (Gelest), TEG (Aldrich) or TBG (Aldrich) in 1:1 weight ratio with TOA or squalene were prepared in an Ar-filled glove box prior to the synthesis and then injected into the flask through a septa lid using a syringe with a long needle immerged into the boiling solvent. The size of the final NCs was controlled by the amount of the precursor injected, which was varied from 0.1 to 1 ml, and by the reaction time, which was changed from a few seconds to 30 min in different experiments. Syntheses were terminated by the removal of heat. After cooling to room temperature, the final solid fraction was separated by centrifuging, washed at least three times with ethanol (for synthesis in TOA), ethylacetate (for squalene) or toluene (for octacosane), and dried under nitrogen. Final powders were dispersed in toluene, ether or dimethylformamide (DMF, $HCON(CH_3)_2$) for further analysis.

Characterization of the samples was made by transmission electron microscopy (TEM) at UC Berkeley using a Tecnai-12 TEM with accelerating voltages of 100kV. High resolution TEM (HRTEM) and elemental analysis were made at Lawrence Livermore Laboratory with a Philips CM300FEG with accelerating voltage of 300 kV. X-ray diffraction (XRD) was acquired using a CPS 120 INEL curved position sensitive detector system utilizing Cu Kα radiation.

Results and discussion.

The boiling points of the solvents used, which are typically listed only for low pressures, were estimated prior to the experiments by measuring the highest temperatures that could be reached in the boiling liquids under Ar flow at ambient pressure. The measured temperatures were 384°C for TOA, 412°C for squalene, and 429°C for octacosane. Additional experiments were made to verify the decomposition temperatures and formation of elemental Ge for each precursor. In these experiments, 1 ml of a precursor was injected at room temperature into an evacuated 250-ml glass flask and heated to the temperature of decomposition, as indicated by formation of a dark solid in the initially colorless vapor. The decomposition of precursors giving a substantial yield of Ge occurred at temperatures of about 140°C for TCG, 390°C for TBG, and 420°C for TEG. One more germanoalkyl, tetramethylgermane, was also tested in preliminary experiments, but was eliminated from further experiments due to its high decomposition temperature of 450°C. Among those precursors tested, TCG had the lowest decomposition temperature. XRD analysis of the final products showed good agreement

4

with the previous data[13], according to which decomposition of TCG above 140°C proceeds with formation of elemental Ge in the following reaction:

$$2HGeCl_3 \rightarrow Ge + GeCl_4 + 2HCl \qquad (1)$$

Taking into account that gaseous HCl and $GeCl_4$ can be easily removed from the reaction at the decomposition temperature, TCG presents special interest as a precursor for solution synthesis of Ge NCs without the formation of any solid byproducts. Test experiments made in the temperature range of 140-300°C confirmed high yield of pure Ge, close to that expected from the reaction (1). When decomposition of TCG was carried out in the absence of any solvents in an evacuated glass flask, black powder heterogeneously formed on the walls of the flask consisting of fully crystalline Ge. However, several attempts to synthesize Ge NCs by homogeneous nucleation from solution in the temperature range of 300-360°C were not successful. Reaction in TOPO did not result in any solid product, while decomposition in TOP yielded mainly amorphous, easily oxidized Ge. The use of TOA at the higher temperature of 380°C enabled synthesis of much better organized nanostructures that were highly resistant to oxidation. The final solid product of the reaction in this case consisted entirely of pure Ge nanoparticles of relatively uniform size (Figure 1). These particles were fully soluble in DMF and ether, but had only partial solubility in toluene and chloroform. It is interesting that deposition from ether typically produced long arrays of particles (Figure 1B), probably due to peculiarities of ether drying on a carbon support film. When the reaction was terminated few seconds after TCG decomposition, the final solid powder consisted only of pure amorphous Ge (XRD spectrum 1 in Figure2). Electron diffraction analysis (insert in Figure 1A) also showed structures close to diamond cubic Ge. However, the

broad diffraction rings still indicated mostly amorphous Ge with only partial

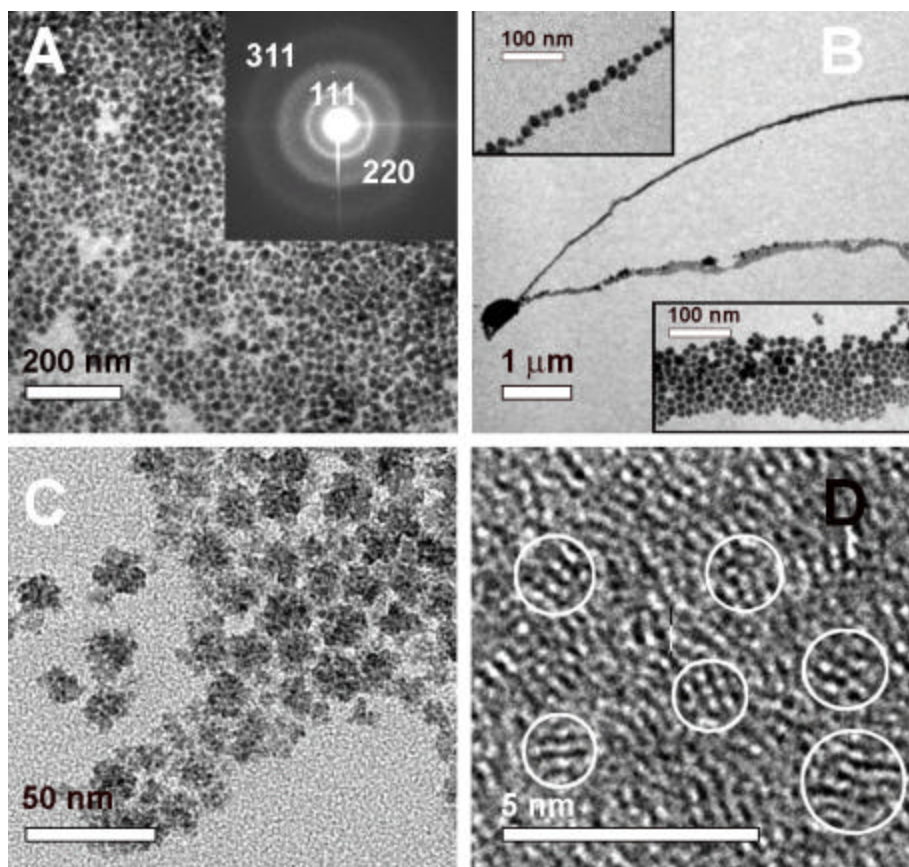crystallographic order. Increasing the reaction time to 30 min resulted in formation

Figure 1 TEM images of Ge nanoclusters formed by decomposition of TCG in TOA at 380°C. (A)-nanoclusters fully dissolved in DMF; diffraction pattern with broad rings (insert) corresponds to average d-spacings close to those of diamond cubic Ge; (B)-long chains obtained from ether solution; inserts show arrays of nanoparticles in the chains; (C) – higher magnification images of the clusters with non-uniform contrast of smaller nanoparticles; (D)-HRTEM image showing partially ordered amorphous structure with inclusions of small nanocrystals (some of them are circled). The distances between clearly distinguished planes are close to that of (111) d-spacing of diamond Ge.

of more organized structures, as indicated by the appearance of non-uniform contrast

seen in the TEM image of Figure 1C and of sharper peaks of crystalline Ge in the XRD

pattern 2 of Figure 2. HRTEM analysis (Figure 1D) confirmed that the TEM contrast and

XRD peaks were determined by the presence of small Ge NCs, with the sizes of 1-2 nm

formed in the initial amorphous matrix. Further increase in the reaction time or the amount of the injected precursor, without increasing of the reaction temperature, did not noticeably affect the size of the crystalline islands, due probably to the exhaustion of the initial precursor.

A substantially higher fraction of crystalline Ge was obtained when TOA was replaced by squalene. In some syntheses conducted below 400°C, XRD analysis still showed an amorphous fraction that essentially disappeared at the boiling temperature of squalene (Figure 2, patterns 3 and 4). Figure 3 A and B shows TEM images of Ge
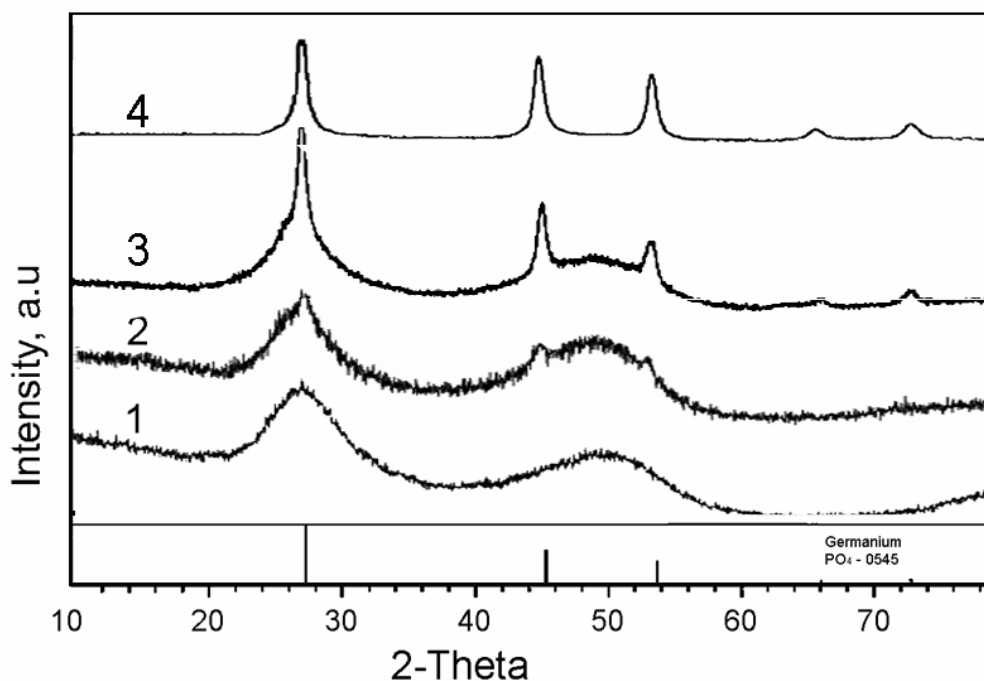

Figure 2. X-ray diffraction patterns of Ge powders obtained by decomposition of TCG: (1)- fully amorphous at 380°C; (2)-amorphous with a fraction of Ge NCs, 380°C; (3)- amorphous with a fraction of Ge NCs, 395°C; (4)-pure crystalline diamond cubic Ge, 410°C. Diffraction patterns similar to (4) were typical for decomposition of all precursors above 410°C.

NCs obtained by decomposition of TCG in squalene at 410°C. Very small NCs, with the sizes of 2-3 nm, were obtained in some syntheses that were continued only for few seconds after decomposition of the TCG injected as a mixture with squalene in the
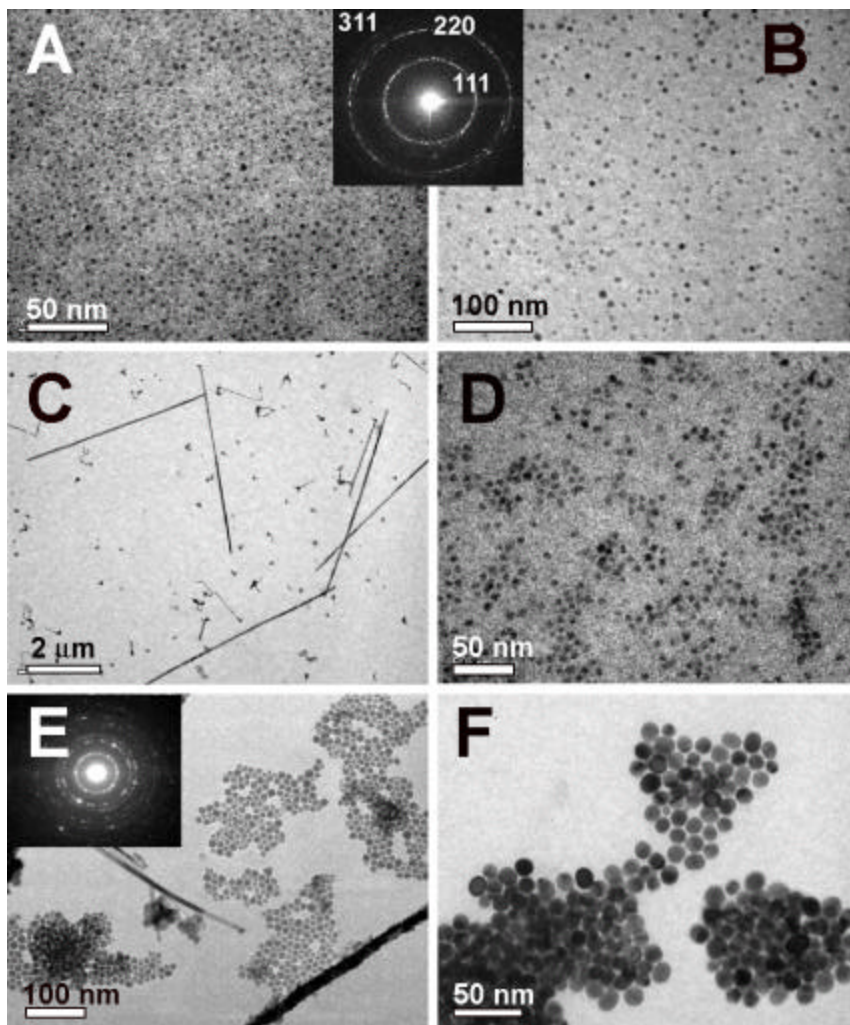

Figure 3. TEM images of Ge NCs by precursor decomposition: (A) and (B) - TCG in squalene at 410°C; (C)-TEG in squalene, 410°C; (D)-TEG in octacosane, 425°C; (E) and (D) – TBG in squalene, 400°C and 410°C, respectively.

amount 0.1 ml. The complication in this case was connected with the strong tendency of Ge to crystallize heterogeneously on the walls of the glass flasks, with formation of large polycrystalline particles. Use of the TCG mixture with TOA in the initial precursor resulted in more controllable homogeneous nucleation in the volume of the solvent, thus

showing the importance of the surfactant choice for controlling the process. Larger NCs were obtained by increasing the amount of injected precursor (0.5-0.9 ml) and reaction time (up to 30 min). In spite of the fact that heterogeneous crystallization on the walls also took place in this case, Ge NCs similar to those shown on the image of Figure 3B could be collected by separation of the soluble part of final product from the main mass of insoluble polycrystalline Ge. In some cases, XRD analysis of the separated part still indicated the presence of small a fraction of amorphous Ge (pattern 3 of Figure 2). However, electron diffraction (insert to Figure 3 A and B) and HRTEM analyses (Figure 4A) clearly confirmed the formation of highly crystalline Ge nanoparticles.

The high boiling temperature of squalene enabled experiments with other Ge precursors, such as TEG and TBG that have higher decomposition temperatures than TCG. Since the decomposition temperature of TEG (420°C) is above the boiling point of squalene, the total yield of Ge with this precursor was relatively low. The final product had a substantial fraction of nanowires (NWs) formed most likely on drops of the boiling solvents condensed on the walls of the flask. The growth mechanism and structure of such NWs has been reported previously.[14] The uniqueness of these NWs is that they form spontaneously in the absence of any crystalline substrates or catalysts that may influence the direction of their growth, as occurs with traditional vapor-liquid-solid (VLS) mechanism. Electron diffraction analysis made with 26 single NWs in the present work confirmed an earlier observation[14] that all straight NWs formed in solution syntheses grew only in [110] direction (Figure 4, B-D). Additional analysis of kinked and branched NWs (Figure 4D) showed that the set of <110> orientations is actually the only directions
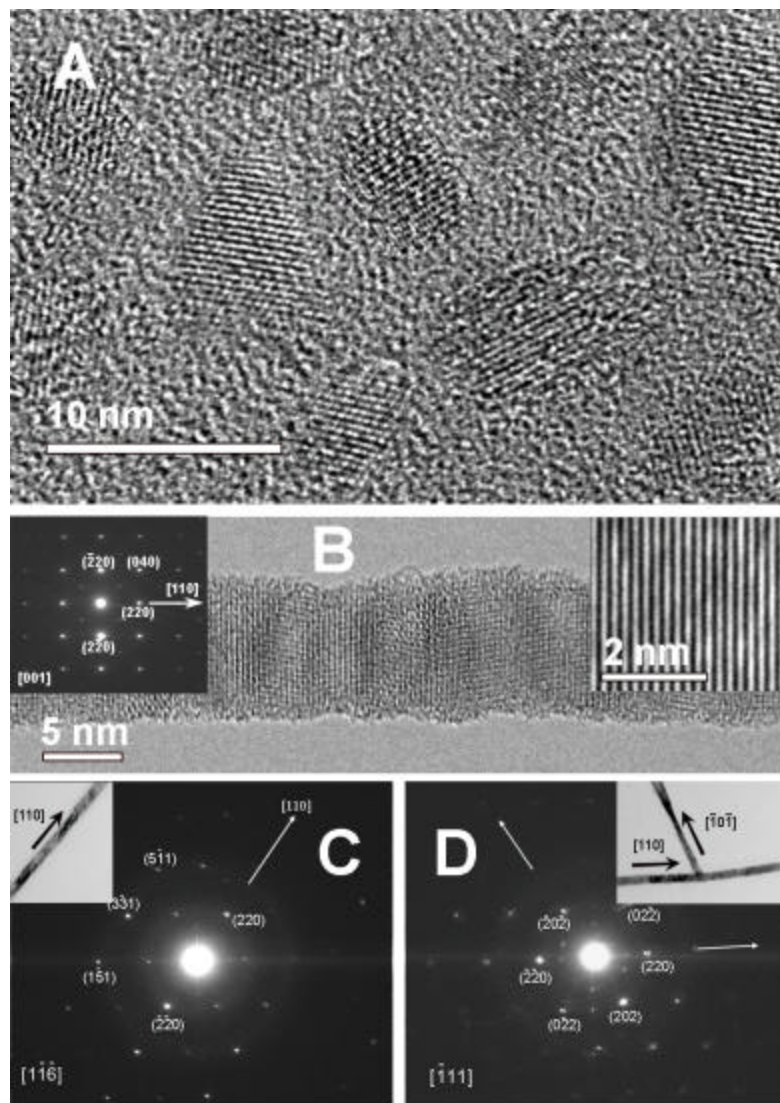
Figure 4. HRTEM images of Ge nanocrystals and obtained by decomposition of TCG (A) and TEG (B) in squalane at 410°C. Diffraction patterns made on single rods showed only <110> direction of growth for both straight (B and C) and branched (D) rods.

of growth for all Ge NWs formed spontaneously in the absence of crystalline substrates or metal catalysts.

A few experiments made with TEG at higher temperatures using octacosane as a solvent showed that decomposition of this precursor can also results in homogeneous nucleation and formation of isometric Ge NCs, requiring however temperatures higher than 420°C (Figure 3D). No polycrystalline Ge formation was observed when 0.5 ml of

pure TEG was injected into boiling octacosane. Size distribution in this case could be controlled relatively well by the duration of the reaction from few seconds to 10 min. The final yield however was also low, due probably to the still low decomposition rate of TEG at the temperature of the reaction.[15] In addition, syntheses in octacosane were complicated because of the difficulties in final NCs purification. Octacosane, that is solid at room temperature, is not soluble in ethanol or ethylacetate, which were used for separation of NCs in syntheses with TOA or squalene. The only solvents found to dissolve octacosane were toluene and chloroform which also partially dissolved small NCs, so a large fraction was lost during the purification procedure due to this mutual solubility.

As mentioned above, among the three alkyl silanes tested in this work, tetrabutyl silane (TBS) has the lowest decomposition temperature of 390°C, suggesting its potential use as a Ge precursor for decomposition on squalene. Figure 3E presents TEM images of Ge NCs obtained in the TBG decomposition experiments when a mixture of TBG with squalene in the amount of 0.6 ml was injected into squalene at 400°C. Sudden decomposition of TBG started only 30 min after the injection, producing isometric NCs with some fraction of NWs. Addition of a small amount of dichlorobenzene to the initial mixture of TBG and squalene produced slightly different NCs (Figure 3F) for the same duration of time. This result indicates the possibility to better tune the size and structure of Ge NCs by variations of surfactants and precursor mixtures, which may be achieved in further studies. It should be noted that, as in the case of TCG, homogeneous formation of NCs in the syntheses with TBG was also accompanied by crystallization of bigger Ge particles on the glass walls. The NCs with relatively narrow size distribution shown in

11

Figure 3 E were separated from the final solid by dissolution in DMF. However, as shown by the image and electron diffraction pattern in the insert, final separated and purified samples still had inclusions of bigger crystals and nanowires showing the need for more experiments to identify the conditions that can limit heterogeneous crystallization on the walls of the reaction vessels.

In conclusion, Ge NCs were synthesized by decomposition of trichlorogermane, tetraethylgermane and tetrabutylgermane. The temperature range of Ge NC colloidal synthesis was extended up to 430°C by use of the high-boiling-point solvents trioctylamine, squalene and octacosane. Trichlorogermane was introduced as a new precursor, decomposing at relatively low temperatures above 140°C, with a high yield of elemental Ge in the absence of any solid byproducts. The results of experiments showed that homogeneous formation of Ge nanoparticles depends on the temperature of TCG decomposition. Purely amorphous structures were obtained below 360°C. Uniform nanoparticles, with inclusions of small Ge NCs having sizes of 1-2 nm formed at 380°C in boiling trioctylamine. Highly crystalline Ge NCs were synthesized in squalene with sizes from 2 nm to 7 nm at increasing temperatures. High boiling points of the investigated solvents enabled studies of other Ge precursors not used previously in colloidal synthesis because of high decomposition temperatures above 390°C. Uniform Ge NCs with sizes from 4 to 15 nm were obtained by decomposition of tetrabutylgermane in squalene. Formation of isometric NCs by decomposition of tetraethylgermane requires higher temperatures, up to 430°C, reached in boiling octacosane. At temperatures below 410°C, decomposition of tetraethylgermane proceeds

with formation of nanowires that were found to grow only in one set of crystallographic

directions <110>.

References

(1) Taylor, B.R.; Kauzlarich, S.M.; Lee, H.W.; Delgado, G.R.; *Chem. Mater.* **1998**, 10, 22-24.

(2) Taylor, B. R.; Kauzlarich, S. M.; Delgado, G. R.; Lee, H. W. H. *Chem. Mater.* **1999**, 11, 2493.

(3) Wilcoxon, J. P.; Provencio P. P.; Samara, G. A.; *Phys. Rev. B* **2001,** 64, 035417 (1-9).

(4) Heath, J.R.; Shiang, J. J. and Alivisatos, A. P.; *J. Chem. Phys.* **1994**, *101*, 1607-1615.

(5) Hope-Weeks, L.J.; Chem.Comm. **2003**, 2980-2981.

(6) Warner, J. H and Tilley, R.D; *Nanotechnology* **2006**, 17, 3745-3749.

(7) Wang, W; Poudel, B.; Huang, J. Y.; Wang, D. Z.; Kunwar, S.; Ren, Z. F.; *Nanotechnology* **2005**, 16, 1126-1129.

(8) Lu, X; Ziegler, K. J.; Ghezelbash, A.; Johnston, K. P.; Korgel, B. A.; *Nano Letters* **2004**, 4, 969-974.

(9) Lu, X.; Korgel, B. A.; Johnston K. P.; *Nanotechnology* **2005**, S389-S394.

(10) Gerion, D; Zaitseva, N.; Saw, C.; Casula, M. F.; Fakra, S.; Van Buuren, T.; Galli, G.; *Nano Letters* **2004**, 4, 597-602.

(11) Lu, X; Korgel, B. A.; Johnston, K. P.; *Chem. Mater.* **2005,** *17,* 6479-6485.

(12) Murray, C.B.; Norris, D.J.; Bawendi, M.G.; *J.Am.Chem.Soc.* **1993**, 115, 8706.

(13) G. Brauer, Handbook of Preparative Inorganic Chemistry, New York: Academic, **1963**.

(14) Zaitseva, N.; Harper, J.; Gerion, D.; Saw, C.; *Applied Physics Letters* **86**, **2005**, 053105.

(15) R.L.Geddes and E.Mack, J. Am. Chem. Soc. **52**, 4372 (1930).